

UNCLASSIFIED

AD NUMBER
AD864678
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 21 Oct 1969. Other requests shall be referred to Air Force Materials Lab., Wright-Patterson AFB, OH 45433.
AUTHORITY
AFML ltr, 7 Dec 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-69-94

AD0864678

OFFICIAL FILE COPY

SILICON-NITROGEN POLYMERS FOR HIGH TEMPERATURE PROTECTIVE COATINGS

A. H. BIRKE, CAPTAIN, USAF

H. ROSENBERG

TECHNICAL REPORT AFML-TR-69-94, (PART I)

OCTOBER 21, 1969

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

BEST AVAILABLE COPY

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

20040303112

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

The distribution of this report is limited because the protection of technical know-how relating to critical products or manufacturing processes, tests and evaluation of military operational weapon systems and installations and other technology is restricted by the U. S. Mutual Security Acts.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

SILICON-NITROGEN POLYMERS FOR HIGH TEMPERATURE PROTECTIVE COATINGS

A. H. BIRKE, CAPTAIN, USAF

H. ROSENBERG

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

FOREWORD

This report was prepared jointly by the Elastomers and Coatings Branch and the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials," and Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734007, "Coatings for Energy Utilization, Control and Protective Functions." This work was administered jointly by Captain A. H. Birke of the Elastomers and Coatings Branch and Dr. Harold Rosenberg of the Polymer Branch, Air Force Materials Laboratory.

This report covers work conducted from January 1967 to December 1967. The report was released by the authors in September 1968 for publication.

This technical report has been reviewed and is approved.



W. P. JOHNSON, CHIEF
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

A laboratory investigation was conducted to develop a synthesis method for the formation of spiro-silicon-nitrogen polymers for potential use as binders in high temperature polymeric protective coatings. Of the various different methods that can be theoretically employed to synthesize spiro cyclodisilazane polymers, this initial work utilized tetrafunctional monomeric silyl amines. Model cyclodisilazane monomers were prepared but attempts to make spiro-trisilazanes and spiro cyclodisilazane polymers were unsuccessful. Results of this preliminary investigation show that this approach, while successful for monomeric cyclodisilazanes, apparently is not suitable for the analogous polymers and that another synthesis route must be developed.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II BACKGROUND	2
III APPROACH	5
1. Monomeric Cyclodisilazanes	5
2. Spiro [3.3] trisilazanes Model Compounds	6
3. Linear Spirosilazane Polymers	8
IV DISCUSSION OF RESULTS	10
1. Monomeric Cyclodisilazanes	10
2. Spiro [3.3] trisilazanes Model Compounds	10
a. Octamethylspiro [3.3] trisilazane	10
b. Attempted Syntheses by Thermolytic Transamination	11
3. Spirosilazane Polymers	13
a. Attempted Syntheses by Thermolytic Transamination	13
b. Attempted Syntheses from Dilithio Anilide and Silicon Tetrachloride	15
V EXPERIMENTAL	16
1. General	16
2. Cyclodisilazanes	18
a. N,N'-Diphenyltetramethylcyclodisilazane	18
b. N,N'-Diphenyltetraphenylcyclodisilazane	18
3. Spirocyclotrisilazanes	19
a. Attempted Synthesis of N,N',N'',N'''-Tetra-ethyltetraphenylspiro [3.3] trisilazane (Without Ammonium Sulfate as Catalyst).	19
b. Attempted Synthesis of N,N',N'',N'''-Tetra-ethyltetraphenylspiro [3.3] trisilazane (With Ammonium Sulfate as Catalyst).	20
4. Spirosilazane Polymers	20
a. Attempted Preparation of Polysprio-N,N'-Dimethylsilazane (By Thermolytic Transamination)	20

TABLE OF CONTENTS (CONTD)

SECTION	PAGE
b. Attempted Preparation of Polyspiro-N, N'- Dimethylsilazane (From Dilithio Anilide and Silicon Tetrachloride)	21
VI CONCLUSIONS	22
REFERENCES	23

SECTION I

INTRODUCTION

As higher speeds are attained by aircraft and other aerospace vehicles, the surface temperature of the craft increases due to aerodynamic heating. Future aeronautical systems capable of sustained high speeds (Mach 3 and greater) are expected to develop surface temperatures of 700°F and higher. Consequently, high temperature protective coating materials are required that will withstand broad temperature extremes. At present no coating is available which possesses the necessary properties of adhesion, flexibility, and long-time thermal stability at temperatures of 700°F and above together with an acceptable method of coating application.

The current state-of-the-art coatings, based on silicone binders, are capable of withstanding extended temperature exposure up to about 650°F, but undergo rather rapid degradation above that temperature. It appears at this time that future coating materials based on the silicones will not be capable of withstanding long-term exposure at temperatures above 650°F (Reference 1). Thus the development of a new polymeric coating material is necessary. It has to have a long-time temperature capability of at least 700°F together with suitable binder characteristics. The polymer system investigated in this research program deals with structures where silicon and nitrogen atoms form the polymer structure backbones.

SECTION II

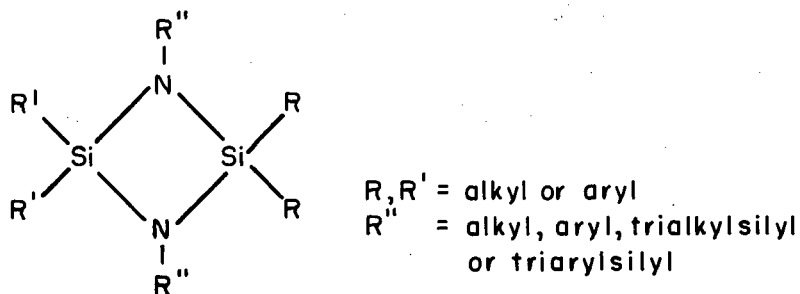
BACKGROUND

The silicon-nitrogen (Si-N) system, on which this research effort was concentrated, is isoelectric with the well known silicon-oxygen (Si-O) compounds but with some important differences. Results of investigations comparing polymers containing Si-O backbones to similar ones with Si-N structures have shown that the latter are more thermally stable (Reference 2).

Theoretically the greater thermal stability of the Si-N bond is explained by the d - p interaction between the silicon and nitrogen atoms resulting from the ability of unshared pairs of electrons of the nitrogen atom to interact with the empty d-orbitals of the silicon. This interaction results in a shorter bond distance and the Si-N bond is rendered more stable.

It is because of this increased stability to thermal degradation that a few polymers containing silicon-nitrogen bonded entities have been investigated for use as high-temperature stable polymeric binders in coating applications (References 3 and 4). A hindrance, however, to a more rapid development of Si-N polymers has been the noted lack of success in preparing high molecular weight linear systems composed entirely of Si-N linkages. Whereas simple linear polymers containing a Si-O backbone can easily be synthesized, similar techniques to produce corresponding Si-N systems usually result in cyclic oligomers (References 5 and 6). However under the proper conditions compounds containing four membered rings or mixtures of compounds containing six and eight membered silicon-nitrogen (silazane) rings can be obtained almost exclusively.

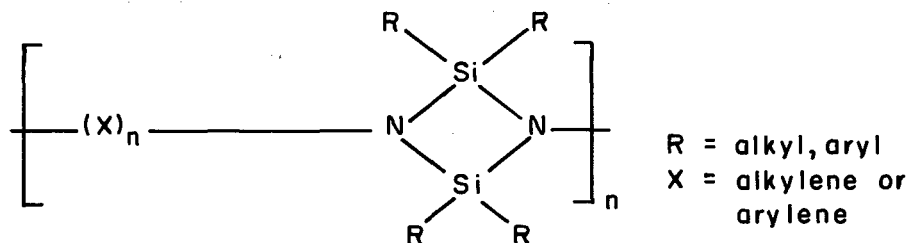
Because of the ease of formation of cyclodisilazanes monomers (four-membered silicon-nitrogen ring compounds) under a variety of conditions (Reference 7) and because of the inherent thermal stability of these compounds



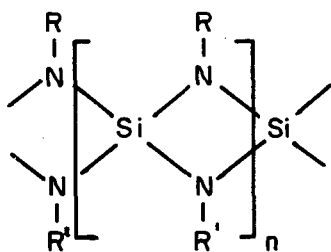
Simple Cyclodisilazane

(Reference 8), the synthesis of polymeric materials incorporating this moiety is very appealing.

One approach to incorporate the cyclodisilazane ring into a linear polymer is by linking individual rings together through the nitrogen atoms of the ring (References 3 and 9). This is shown below.



Another approach would be to link the cyclodisilazane units together through the silicon atoms in such a manner so as to transform the resulting polymer into a linear spiro chain.



$R = \text{alkyl, aryl, trialkylsilyl or triarylsilyl}$

$R' = \text{same as or different from } R$

Basic Mer Unit of a Spiro Silazane Polymer

This polymer incorporates not only the inherent thermal stability of the Si-N linkage but also the added stability provided by the spiro structure.

The spiro structure, as well as the analogous ladder structure in polymer design (e.g. ladder pyrones, phenyl-T, black orlon, etc), is theoretically predicted to have a greater degree of thermal stability than the simple single strand polymers (Reference 10). This stability derives from the fact that in the double-stranded polymer, two bonds must be broken simultaneously in the same "block" of the (double stranded) polymer backbone before the polymer chain is severed. A single strand polymer on the other hand, is cleaved with loss of physical and mechanical properties when only one bond is broken in the backbone. Since the chances for simultaneous rupture in the ladder or spiro polymer are statistically low, the polymer retains its properties at higher temperatures than its single stranded counterpart because it remains intact. This theoretical prediction has been experimentally verified in various double stranded polymer systems (Reference 11).

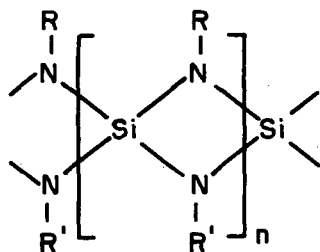
To date, no one has reported any research endeavor which attempts to produce a double stranded spiro polymer whose backbone consists entirely of Si-N linkages. The preparation of such a polymer is the object of this program.

SECTION III

APPROACH

The fundamental approach taken for the synthesis of thermally stable Si-N polymers consisted of the following phases:

1. Preparation of monomeric cyclodisilazane model compounds.
2. Synthesis of spirotrisilazane model compounds.
3. Synthesis of spiro Si-N polymers of the general structure.



R = alkyl, aryl, trialkylsilyl or triarylsilyl

R' = same as or different from R

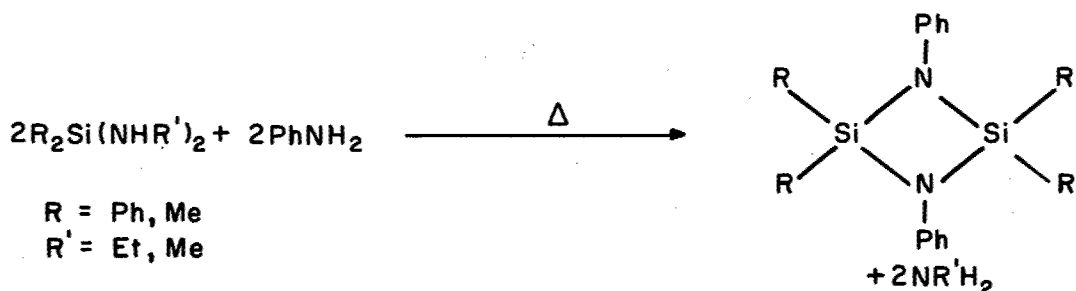
Basic Unit of a Four-Membered Si-N Spiro Polymer

4. Comprehensive survey of the cyclodisilazane literature.

Each of these phases will be covered with the exception of the literature survey.

1. MONOMERIC CYCLODISILAZANES

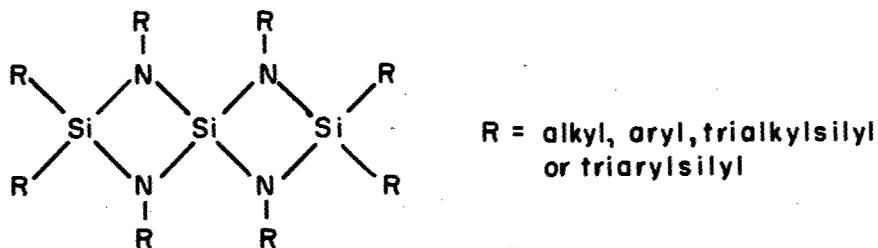
Although numerous methods have been reported for the preparation of cyclodisilazanes (Reference 2), the method employed in this effort was thermolytic transamination (Reference 12).



This method was chosen because the yields of product were reported to be very high, the products usually of high purity (the liberated amine is easily removed by distillation), and because of the desired advantages deriving from the use of a reaction of this type in the synthesis of polymers, i.e., high yields of pure products.

2. SPIRO [3.3] TRISILAZANES MODEL COMPOUNDS

The synthesis of these compounds was undertaken in order to obtain and

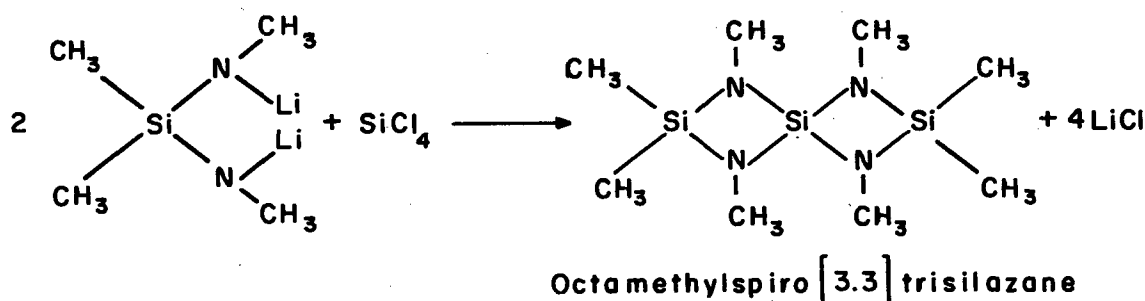


Basic Spiro [3.3] trisilazane Structure

study the infrared (IR) spectra of these spiro four membered Si-N rings so as to compare this data with that derived from the simple mono-cyclodisilazanes. The IR region between 870 to 900 cm^{-1} was closely analyzed to determine whether or not absorptions occurred in this range in the spiro as well as in the monocyclic silazanes. This region of the IR has been associated with the cyclodisilazane ring in the monocyclic compounds by Breed (Reference 7). Thus, if this absorption was present in the spiro compounds, it probably would be present in spiro polymers. In this way a simple observation of the IR spectra

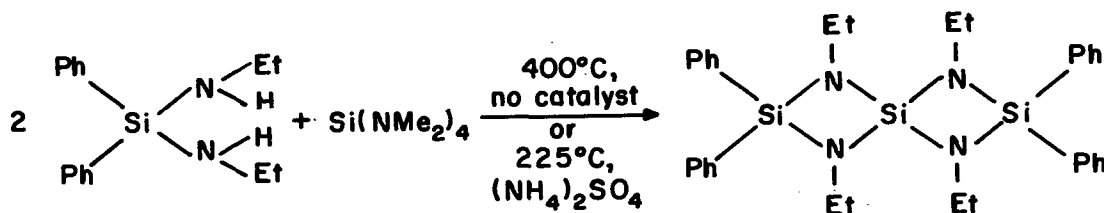
of products resulting from future polymer syntheses would show whether or not cyclodisilazane rings were present.

To date, only one spirotrisilazane has been reported (Reference 13). This compound, octamethylspiro [3.3] trisilazane (below), was reported by Lienhard and Rochow and was prepared by the reaction of the dilithium salt of N,N -bis (methylamino)dimethylsilane and silicon tetrachloride.



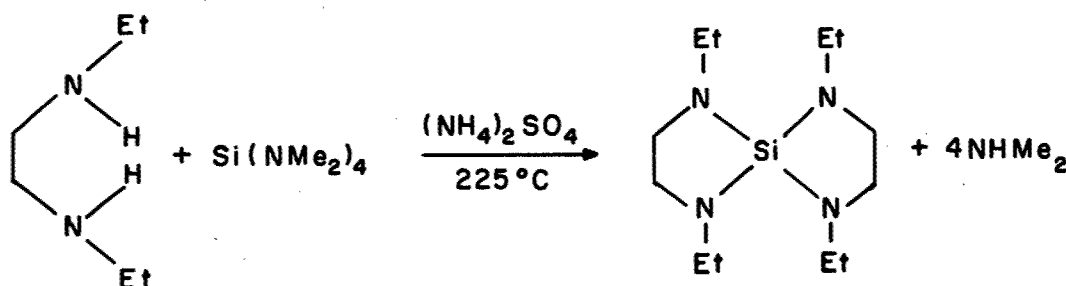
In the program reported herein, it was planned to repeat this particular synthesis and to produce related spiro compounds by this method.

It was also planned to develop these spiro compounds by utilizing thermolysis methods analogous to the transamination reaction used for producing monomeric cyclodisilazanes. For example, the reaction of two moles of a bis(alkylamino)dialkylsilane with one mole of a tetrakis(dialkylamino)silane should theoretically yield a spirotrisilazane if the qualification is made that the bis(alkylamino)dialkylsilane does not react intramolecularly with itself to produce the simple cyclodisilazane



Another approach to the same material was based on a low temperature, ammonium sulfate-catalyzed transamination reaction analogous to a procedure

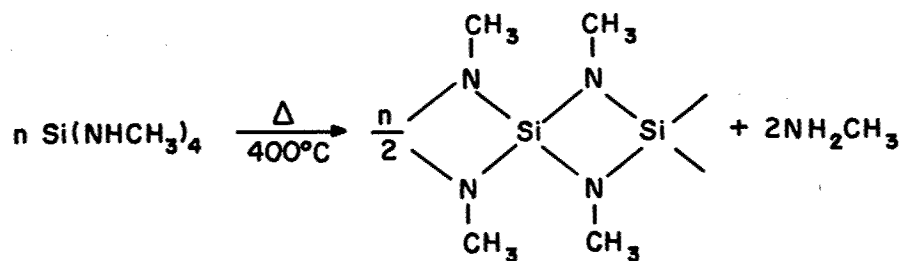
reported by Yoder and Zuckerman (Reference 14) and Able and Bush (Reference 15). The latter pair reported the spiro compound shown below made from 1,2-bis(ethylamino)ethane and tetrakis(dimethylamino)silane using ammonium sulfate as a catalyst.



3. LINEAR SPIROSILAZANE POLYMERS

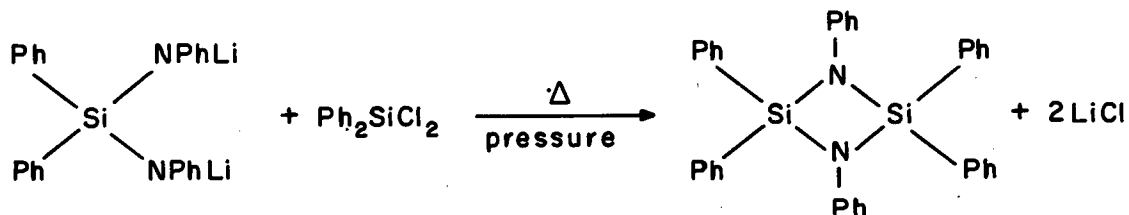
Two methods of approach were envisioned to produce a linear silicon-nitrogen spiro polymer.

One method utilized the basic thermal transamination reaction employed for the preparation of mono-cyclodisilazanes. Thus with tetrakis(methylamino)silane the following reaction was planned:

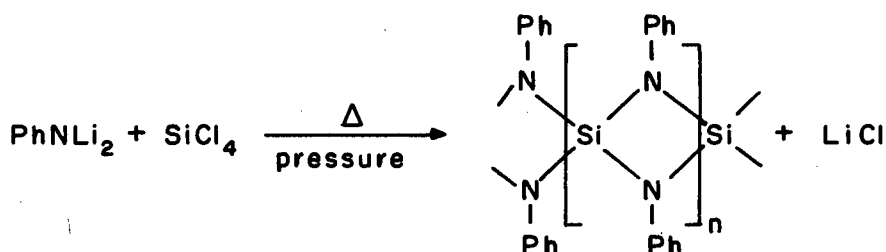


The possible disadvantage of the method lies in the fact that cross-linking rather than straight linear polymer formation, will produce intractable gels or infusible and insoluble solids. However, since the reaction is easily carried out, it was included as an attempted method of preparation due to the many potential advantages deriving from such a straightforward method.

The second method was based on a procedure utilized by Fink (Reference 16) for the preparation of N,N'-(diphenyl)tetraphenylcyclodisilazane (hexaphenylcyclodisilazane). The dilithium salt of bis(anilino)diphenylsilane was heated with diphenyldichlorosilane.



The postulated reactants in our attempt were to be dilithio anilide and silicon tetrachloride.



In this method the possibility of cross-linking occurring made the preparation of a linear polymer questionable.

SECTION IV

DISCUSSION OF RESULTS

1. MONOMERIC CYCLODISILAZANES

These preparations, described in detail in the Experimental Section, were easily carried out and the yield of crude product was always very high. From these experiments it was concluded that thermolytic transamination reactions were definitely a desirable procedure to use for the synthesis of cyclodisilazane rings if the method was applicable to the product desired. The crude crystalline products resulting from the reactions were easily purified to analytical quality by two or three recrystallizations. Their IR and NMR spectra were recorded and studied. From the IR data of these and other cyclodisilazanes reported in the literature, it was observed that absorptions in the IR region between 870 to 900 cm^{-1} are characteristic only of cyclodisilazanes. Other cyclic silazanes and linear silicon-nitrogen containing monomers and polymers do not absorb in this region. From these observations it was concluded that this feature of the IR spectrum could be used to identify the presence of the four-membered cyclodisilazane ring whether it existed by itself or as a part of a larger silicon-nitrogen compound or mixture. Whether this identifying feature remained in spiro four-membered silazanes had not been demonstrated at the time this investigation was initiated. Thus the synthesis of these was a desired next step in the program.

2. SPIRO 3.3 TRISILAZANES MODEL COMPOUNDS

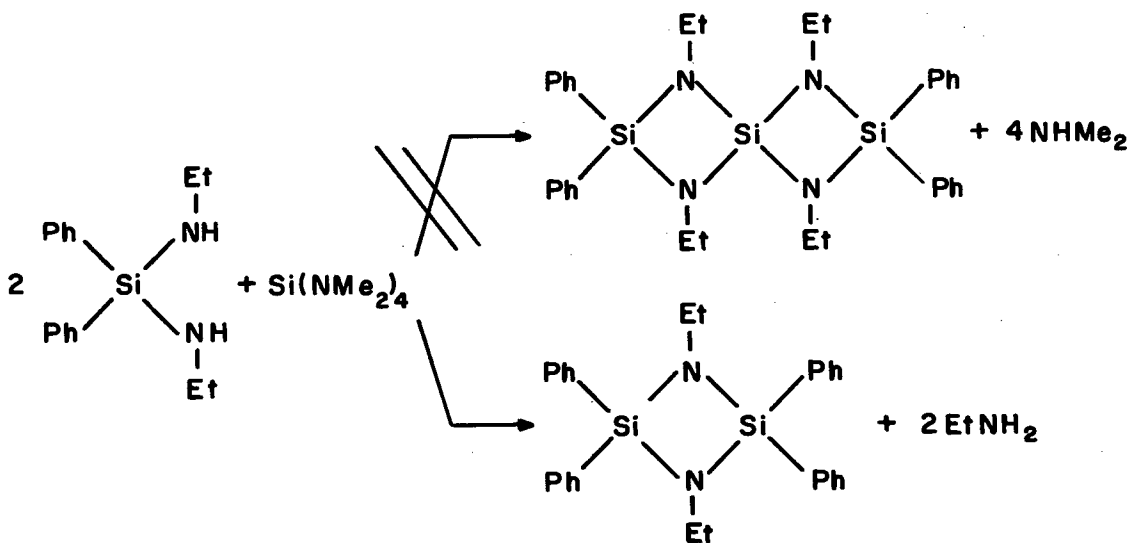
a. Octamethylspiro [3.3] trisilazane

Numerous attempts to repeat the synthesis of octamethylspiro [3.3] trisilazane according to the procedure reported by Lienhard (Reference 13) were unsuccessful. No spiro material was isolated and only mixtures of high boiling polymeric silazanes were obtained. Similar results were found with other bis(alkylamino)dialkylsilane homologues (e.g. bis(ethylamino)diphenylsilane and bis(ethylamino)diethylsilane using this same procedure).

Private communications with Lienhard indicated that he had never repeated the synthesis; however, he offered suggestions and modifications which might make repeating the procedure possible, e.g., using a different solvent than that mentioned in the literature on his synthesis and also employing a higher dilution. A repeat of this procedure employing these suggestions has not yet been attempted.

b. Attempted Syntheses by Thermolytic Transamination

The attempts to obtain a spirotrisilazane by thermolytic transamination gave not the desired compound but the simple mono-cyclodisilazane



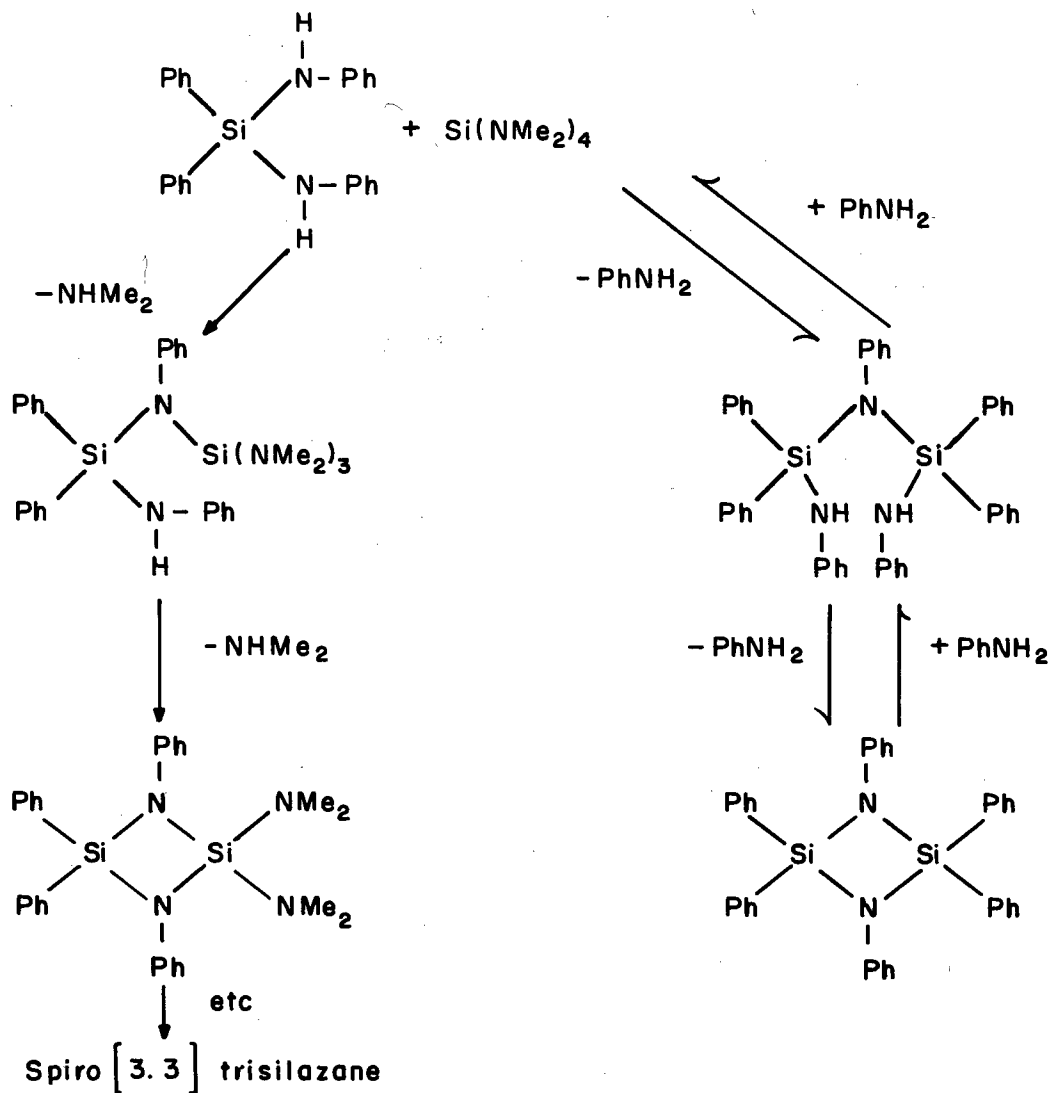
In the reaction run at temperatures up to 450°C without catalyst the yield of cyclodisilazane, N,N'-diethyldiphenylcyclodisilazane was 45% (calculated on the basis that all of the starting material, bis(ethylamino)diphenylsilane, was available for cyclodisilazane formation).

From the major reaction product isolated it is seen that the complete reaction between two molecules of the bis(ethylamino)diphenylsilane occurred before reaction between the above molecule and the tetrakisaminosilane could occur. The former reaction liberates a molecule of ethylamine and, since it is a gas, it immediately leaves the reaction mixture. Thus, once the formation of

the cyclodisilazane has occurred, there is no chance for reaction with the tetrasubstituted silane because no ethylamine is present to reverse the formation of the monocyclic silazane and intermediates thereof.

It is speculated that a reaction of this type might succeed to give a spiro compound rather than the cyclodisilazane if the bis(primary amino)dialkyl(aryl) silane used was a molecule such as bis(anilino)diphenylsilane. In this case, since the transamination reactions are reversible, the spiro compound might be formed if the reaction temperature is kept below the boiling point of the aniline which would be released in the competitive cyclodisilazane formation. Since the liberated dimethylamine would be irreversibly removed from the reaction mixture as a gas, theoretically the spiro compound could possibly be formed because the aniline would be available to reverse the formation of the cyclodisilazane and its intermediates.

In the reaction between the bis(ethylamino)diphenylsilane and tetrakis(dimethylamino)silane which was run at 225°C with ammonium sulfate as a catalyst, once again N,N'-diethyltetraphenylcyclodisilazane was the only product isolated. The yield was lower than that obtained in the high-temperature reaction without a catalyst.

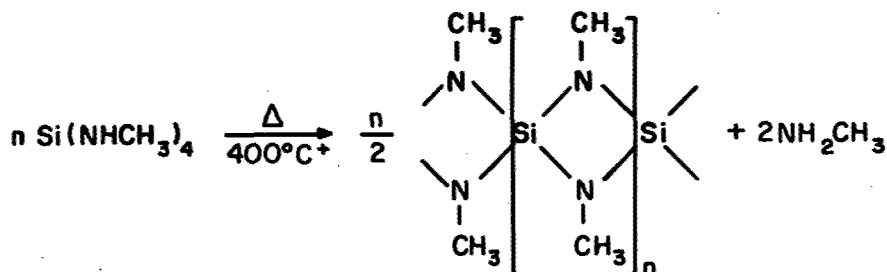


3. SPIROSILAZANE POLYMERS

a. Attempted Syntheses by Thermolytic Transamination

As mentioned in the discussion of simple cyclodisilazanes, this method was investigated as a spiro polymer preparation because it basically involves the same reaction as that used to obtain cyclodisilazanes. It therefore has the

potential advantages of being easy to carry out and of providing high purity products in good yields. The reaction investigated was the following:



In the experiment it was observed that about one-eighth of the total amount of methylamine expected for the complete formation of the spiro polymer was evolved after 26 hours heating at pot temperatures between 250 to 300°C. The material in the reaction flask consisted of a clear gel at this stage.

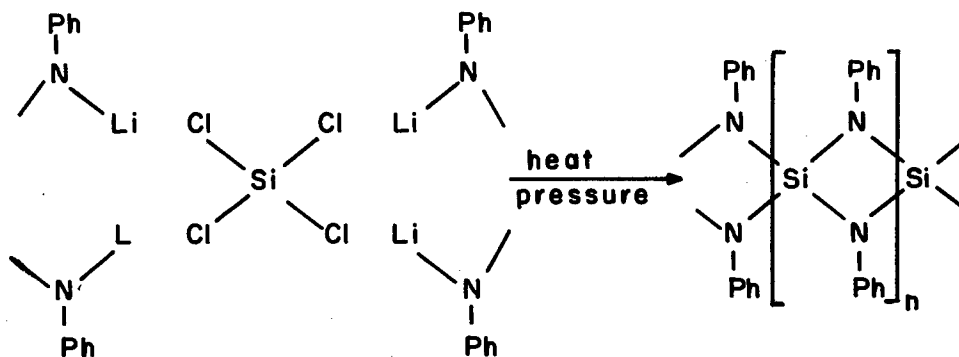
Further heating at a pot temperature of 390°C for ten hours resulted in the previously fluid mass suddenly solidifying to a white foam-structured solid. The amount of amine liberated at this point amounted to approximately two-fifths of the theoretical. Continued heating at pot temperatures up to 410°C led to the expulsion of a little more amine but the total was far less than the theoretical.

The resulting yellow, brittle polymer was insoluble in all organic solvents checked, resistant to acid hydrolysis and infusible. Undoubtedly the material was an incompletely cross-linked polymer but not the linear variety desired.

If the formation of rings as required for the spiro polymers were not favored kinetically, cross-linked product would predominate even though the four-membered rings are thermodynamically more stable. This would happen because the loss of liberated amine makes the initial reaction irreversible. Thus the simple four membered silazane spiro polymer cannot be obtained. It appears at this time that a simple thermolytic transamination reaction will not work when the probability for cross-linking is just as great as linear spiro chain formation.

b. Attempted Synthesis from Dilithio Anilide and Silicon Tetrachloride

In this attempted preparation the dilithio anilide and silicon tetrachloride were reacted in a 2:1 ratio with the expectation that the formation of the four membered ring would be favored over cross-linking and a linear spiro polymer obtained.



In the one complete reaction tried, however, the only identifiable products recovered after removal of the lithium chloride by washing with water were siloxanes. A leak developed in the autoclave in the second run and the reaction has not been repeated.

SECTION V

EXPERIMENTAL

1. GENERAL

The solvents used were dried by distillation from lithium aluminum hydride, molecular sieves, or by passage of the distilled vapors through molecular sieves. The solvents were used as quickly as possible after distillation. If the dried solvent could be directly distilled into the reaction flask this was the preferred method.

Glassware was heated in an oven held at 125°C and assembled immediately after removal from the oven. All set ups were pre-swept with nitrogen. The nitrogen employed was G. E. Lamp Grade. This was further purified by bubbling through a scrubber containing Fieser's solution to remove any residual oxygen and then through concentrated sulfuric acid to remove any traces of water. A drying tube containing pellets of sodium hydroxide was placed in the gas line after the acid bath to neutralize any acid fumes that might be swept along.

The apparatus employed for the thermolytic transamination reactions is shown in Figure 1. The reaction flasks used were of Pyrex for reaction temperatures below 400°C and of quartz for higher temperature reactions. This set-up was connected directly by tubing to an acid bath which neutralized the liberated amines. A small stream of nitrogen was used to carry the amine gases to the acid bath.

Elemental analyses were performed by Spang Laboratories, Ann Arbor, Michigan unless noted otherwise.

Molecular weights were determined using high resolution mass spectroscopy by Mellon Institute.

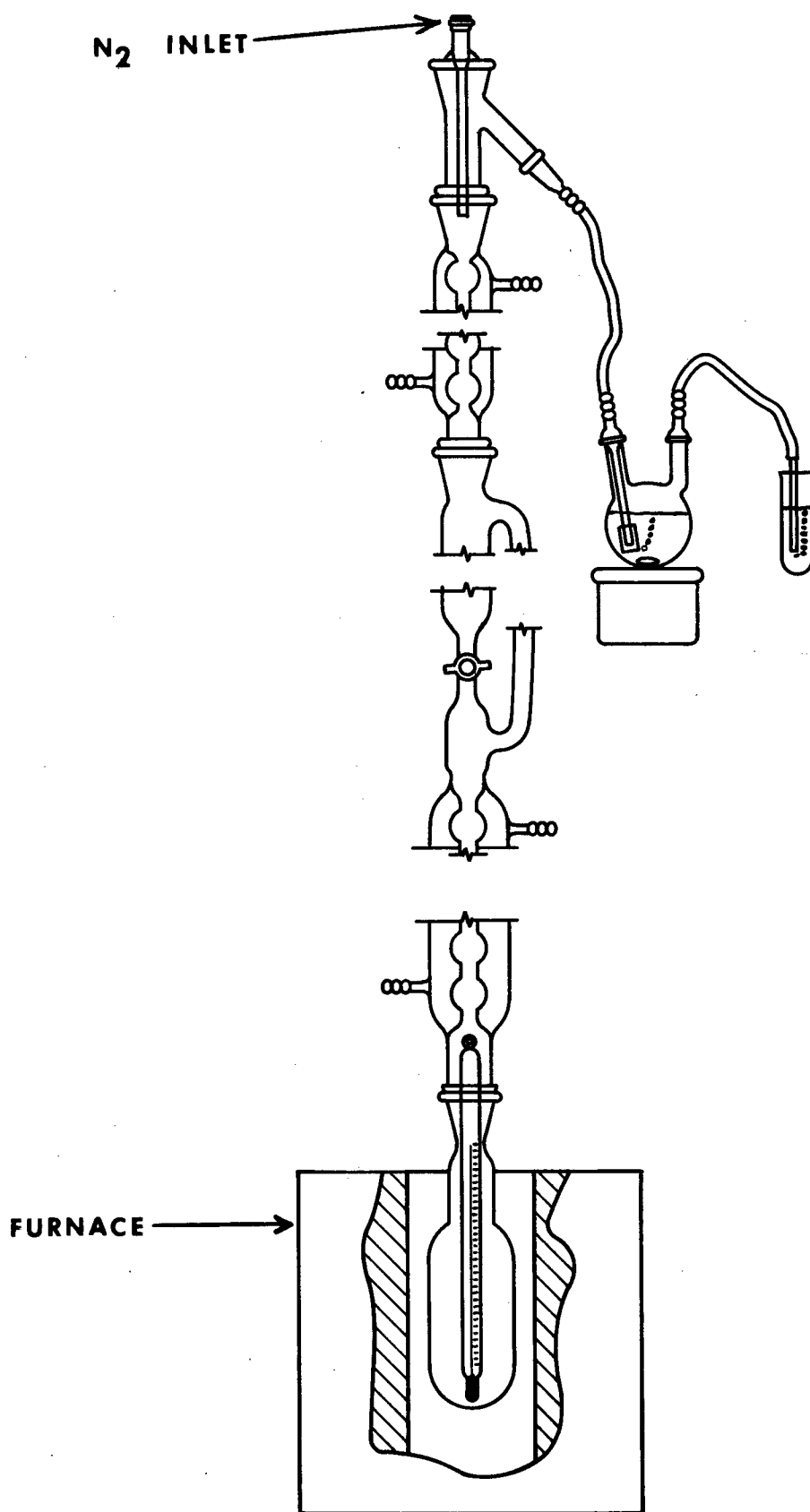


Figure 1. Schematic Apparatus for Preparation of Cyclodisilazanes by Thermolytic Transamination

2. CYCLODISILAZANES

a. N,N'-Diphenyltetramethylcyclodisilazane

The reaction apparatus used was that illustrated in Figure 1. The scrubber flask contained 0.65 mole of hydrochloric acid solution. The reactants, 28.39g (0.24 mole) of freshly distilled bis(methylamino)dimethylsilane (n_D^{25} 1.4112) and 22.38g (0.24 mole) of aniline, were added together in a 200 ml Kjeldahl-type flask (Figure 1) in a dry box. The stoppered flask was removed from the dry box and quickly connected to the upper apparatus which had been purged for 20 minutes with a stream of nitrogen. A slow stream of nitrogen was maintained throughout the reaction.

Methylamine evolution began immediately on heating the reaction flask and the temperature in the flask climbed steadily to 200°C. At this temperature rapid condensation in the lower condenser prevented the refluxing materials from reaching a higher temperature. Water flow in the lower condenser was discontinued and the water removed.

Then the temperature in the pot steadily climbed as the lower boiling material was liquified in the upper condenser and collected in the addition funnel. At 300°C the liquid in the funnel was allowed to stream, dropwise, into the pot. This lowered the temperature somewhat initially but by maintaining a slow addition rate the lower boiling intermediates continued recycling until they reacted. After about 20 hours of continued heating a pot temperature of 350°C was reached and heating was discontinued. The amount of methylamine neutralized indicated that 89% of the theoretical amount had been liberated. The crude yield of cyclodisilazane was 28.6g (80%). This material was recrystallized from benzene and dried at 70°C in vacuo, mp 251.5-252.5°C. Reported (Reference 12) 252.5°. Calcd for $C_{16}H_{22}Si_2N_2$: C, 64.37; H, 7.43; N, 9.39; Si, 18.81; mol wt, 298.1322. Found: C, 64.31; H, 7.39; N, 9.41; Si, 18.92; mol wt, 298.1320.

b. N,N'-Diphenyltetraphenylcyclodisilazane

The same apparatus and procedure used in the synthesis of N, N -diphenyl-tetramethylcyclodisilazane was used for the preparation of the hexaphenyl

analog. The reactants were freshly distilled and consisted of 44.67g (0.165 mole) of bis(ethylamino)diphenylsilane and 15.38g (0.165 mole) of aniline. The reaction flask was heated until a temperature of 500°C was reached in the reactants. (Note: There was no need for recycling as in the previous experiment as no low boiling intermediates were produced). Total heating time was 5 hours.

On cooling the light yellow colored material in the flask solidified. Hexane was added and after thorough stirring the crystals were collected by filtration. The yield was 41.8g (92%), mp 345-351°C. After two recrystallizations from bromobenzene, the resulting white crystals were dried in vacuo at 100°C, mp 354.5-356°C. Reported mp (Reference 12) 355.5°C.

Calcd for $C_{36}H_{30}Si_2N_2$: C, 79.07; H, 5.53; N, 5.12; Si, 10.27; mol wt, 546.1946. Found: C, 78.96; H, 5.77; N, 4.99; Si, 10.79, mol wt, 546.1951.

3. SPIROCYCLOTRISILAZANES

a. Attempted Synthesis of N,N',N'',N'''-Tetraethyltetraphenylspiro [3.3] trisilazane (Without Ammonium Sulfate as catalyst)

Using the same apparatus as in the above two syntheses, the freshly-distilled reactants, bis(ethylamino)diphenylsilane, 27.04g (0.10 mole) and tetra-kis(dimethylamino)silane, 10.22g (0.05 mole) were heated as before. The evolved amine was neutralized by a hydrochloric acid solution of known concentration.

By recycling the lower boiling intermediates as in the first synthesis, a pot temperature of 450°C was eventually attained. This took about 20 hours.

On cooling, the reaction mixture solidified and the light yellow colored solid was collected, recrystallized from benzene and dried in vacuo. Yield 10.1g, mp 197°-199°C. After studying the IR and NMR spectra of this compound and comparing these results with the data on N, N -diethyltetraphenylcyclodisilazane reported by Fink (Reference 12) it was concluded that the product was the cyclodisilazane, Fink reported, mp 195-96°C. The yield of recrystallized material (mp 197-99°C) was 45% on the basis that all of the bis-(ethylamino) diphenylsilane was available for cyclodisilazane formation. The amount of

hydrochloric acid solution neutralized indicated a 78% reaction assuming that all the amine liberated was diethylamine.

b. Attempted Synthesis of N,N',N'',N''' -Tetraethyltetraphenylspiro[3.3] trisilazane (With Ammonium Sulfate as a Catalyst)

In a nitrogen purged reaction system, consisting of a 150 ml flask and simple condenser and connected via tubing to a hydrochloric acid scrubber containing a known amount of acid, was placed the same amounts of material as in the preceding reaction along with 0.01g of ammonium sulfate. A continuous nitrogen flow was maintained and the flask was heated at 225°C in an oil bath for 36 hours.

On cooling a precipitate formed. This was purified and found to be identical with the N,N'-diethyltetraphenylcyclodisilazane obtained in the preceding experiment.

The amount of HCl neutralized corresponded to a 38% conversion assuming that all the liberated amine was diethylamine. The amount of material isolated was about 4 grams.

4. SPIROSILANAZE POLYMERS

a. Attempted Preparation of Polyspiro-N,N'-Dimethylsilazane (By Thermolytic Transamination)

Using the same reaction apparatus as in 2a, 44.49g (0.030 mole) of tetra-kis(methylamino)silane was initially heated for 8 hours at 290°C (pot temperature), 16 hours at 250°C and 2 more hours at 300°C. On cooling a clear gel formed and it was determined that 15% of the theoretical amount of methylamine (necessary for complete spiro polymer formation to occur) had been liberated.

The flask was reheated for ten additional hours at 390°C. On cooling, the reactant material appeared as a white foam-structured solid along with small amounts of liquid. Amine liberated (total) was 38% of theoretical. Further

heating at 410°C for 12 hours resulted in a 42% liberation of amine. The material was yellow colored at this time indicating that decomposition was occurring.

The resultant brittle yellow crystalline material was insoluble and infusible. It was finely ground in a mortar, washed with various solvents and dried in vacuo. However, even after repeated washings a residual ammoniacal odor persisted. On heating, the material slowly darkened above 400°C but did not melt by 450°C. An IR spectrum of a Nujol mull of this material revealed the presence of unreacted N-H. Calcd for $(C_{12}H_{10}N_2Si)_n$: C, 27.88; H, 7.02; N, 32.51; Si, 32.59. Found (Spang Lab) C, 21.41; H, 7.01; N, 28.70; Si, 32.08; (E. I. Robertson) C, 24.01; H, 6.53; N, 26.93.

b. Attempted Preparation of Polyspiro-N,N'-Dimethylsilazane (from Dilithio Anilide and Silicon Tetrachloride)

In a 11. flask equipped with a condenser and prepurged with nitrogen was prepared dilithioanilide from 27.94g (0.3 mole) of aniline and 0.06 mole of 1.67 N n-butyllithium in hexane.

To the resulting white suspension, which had been cooled to 0°C in an ice-bath, was added dropwise 22.09g (0.13 mole) of silicon tetrachloride. The resulting mixture was refluxed for 19 hours at atmospheric pressure under nitrogen and then heated for 12 additional hours in a stirred Parr pressure reaction apparatus. The temperature attained was 260°C at 280 PSI.

After removal of the reaction contents from the high pressure apparatus and filtering, the light tan residue which had been collected was refluxed with water to remove the lithium chloride from the product. The resulting gray solid material was studied by IR spectroscopy and it was found to consist almost entirely of silicon-oxygen containing materials. No pure silicon-nitrogen materials were isolated.

The second attempted preparation failed when a leak developed in the Parr apparatus.

SECTION VI

CONCLUSIONS

Cyclodisilazanes represent a class of polymers having potential as binder materials in high temperature polymeric protective coatings. This has been demonstrated by preliminary investigations of polymeric coating materials containing the cyclodisilazane moiety and by independent thermal stability studies of silicon-nitrogen containing materials. Based on initial results obtained in this program, it is concluded that methods employing tetrafunctional monomeric silyl amines, while suitable for the synthesis of monomeric cyclodisilazanes, are apparently not applicable for the formation of the analogous spiro silicon-nitrogen polymers. Future work thus will concentrate on other theoretically feasible routes to the spiro cyclodisilazane polymers.

REFERENCES

1. R. L. Stout, Air Force Materials Laboratory, AFML-TR-67-433 (1968).
2. E. G. Rochow, *Monatsh. Chem.*, 95, 750 (1964).
3. J. M. Butler and C. E. Hathaway, Monsanto Research Corporation, AFML-TR-65-3 (1965).
4. R. E. Burks, Jr., R. E. Lacy, and C. L. Cristy, Jr., U. S. Patent 3311571 (1967).
5. E. G. Rochow, *Pure Appl. Chem.*, 13, 247 (1966).
6. B. J. Aylett in "Preparative Inorganic Reactions," Vol II, W. L. Jolly, Ed., Interscience, New York, N. Y., 1965.
7. L. W. Breed and R. L. Elliott, Midwest Research Institute, AFML-TR-66-116, Part II (1967).
8. W. Fink, *Angew. Chem. (Int. Ed.)*, 5, 760 (1966).
9. W. Fink, *Helv. Chim. Acta.*, 49, 1408 (1966).
10. M. L. Tessler, Air Force Materials Laboratory, ML TDR 64-151 (1964).
11. A. A. Volpe and W. J. Bailey, United States Naval Ordnance Laboratory, NOLTR 66-120 (1966), AD 641873.
12. W. Fink, Belgian Patent 630,249 (1963).
13. K. Lienhard and E. G. Rochow, *Z. Anorg. Allg. Chem.*, 331, 316 (1964).
14. C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, 88, 4831 (1966).
15. E. W. Able and R. P. Bush, *J. Organometal. Chem.*, 3, 245 (1965).
16. W. Fink, *Helv. Chim. Acta.*, 47, 498 (1964).

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

SILICON-NITROGEN POLYMERS FOR HIGH TEMPERATURE STABLE COATINGS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

January 1967 - December 1967

5. AUTHOR(S) (First name, middle initial, last name)

August H. Birke, Capt., USAF
Harold Rosenberg

6. REPORT DATE

September 1969

7a. TOTAL NO. OF PAGES

30

7b. NO. OF REFS

16

8a. CONTRACT OR GRANT NO.

b. PROJECT NO. 7342, 7340

c. TASK NO. 734201, 734007

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

AFML-TR-69-94, (Part I)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Air Force Materials Laboratory
Wright-Patterson AFB, Ohio 45433

13. ABSTRACT

A laboratory investigation was conducted to develop a synthesis method for the formation of spiro-silicon-nitrogen polymers for potential use as binders in high temperature polymeric protective coatings. Of the various different methods that can be theoretically employed to synthesize spiro cyclodisilazane polymers, this initial work utilized tetrafunctional monomeric silyl amines. Model cyclodisilazane monomers were prepared but attempts to make spiro-trisilazanes and spiro cyclodisilazane polymers were unsuccessful. Results of this preliminary investigation show that this approach, while successful for monomeric cyclodisilazanes, apparently is not suitable for the analogous polymers and that another synthesis route must be developed.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

UNCLASSIFIED

Security Classification

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Polymer Silicon-Nitrogen Coatings						

UNCLASSIFIED

Security Classification